

Geochemical Profiles Across the Listvenite- Metamorphic Transition in the Basal Megathrust of the Semail Ophiolite: Results from Drilling at Oman DP Hole BT1B

M. Godard^{1*}, E. Carter², R. Lafay¹, E. Bennett³, F. Kourim⁴, J.-C. de Obeso⁵, K. Michibayashi⁶, M. Harris⁷, J. Coggon⁸, D. Teagle⁸, P. Kelemen⁵ and the Oman Drilling Project Phase 1 Science Party

¹ Géosciences Montpellier, CNRS, Université de Montpellier, Montpellier, France

² University of Manchester, Department of Earth and Environmental Sciences, Manchester, United Kingdom

³ Cardiff University, Earth and Ocean Sciences, School of Earth and Ocean Sciences, Cardiff, United Kingdom

⁴ Academia Sinica, Institute of Earth Science, Taipei, Taiwan

⁵ LDEO, Columbia University, Palisades, NY, United States

⁶ Dep. Earth and Planetary Sciences, Graduate School of Environmental Studies, Nagoya University, Nagoya, Japan

⁷ School of Geography, Earth and Environmental Sciences, Plymouth University, Plymouth, United Kingdom

⁸ School of Ocean & Earth Science, University of Southampton, United Kingdom

Contents of this file

Text S1. Analytical Methods

Text S2

Figures S1 to Sx

Additional Supporting Information (Files uploaded separately)

Captions for Tables S1 to S3

Caption for Dataset S1

Introduction

Supporting information comprise a detailed description of the analytical techniques used to acquire the dataset presented in this article ([Text S1 and Table S1](#)), the compiled composition shown for comparison in Figures 2 and 3 ([Table S2](#)), and used for mass balance calculations ([Table S3](#)) and the details of the method used for mass balance calculations ([Text S2](#)). The lithology and depth of the studied samples and their major, trace and volatile element concentrations are reported as [Supplementary Dataset S1](#).

Text S1. Analytical methods

The major element composition of Hole BT1B samples was determined by X-ray fluorescence (XRF) on-board D/V Chikyu for the drillsite and shipboard samples and at GeoLabs (Ontario, Canada) for consortium samples. The volatile element composition of the drillsite and shipboard samples was determined by combustion CHNS elemental analysis (EA) and coulometry on-board D/V Chikyu. The trace element composition of the drillsite, shipboard and consortium samples was analyzed by Inductively-Coupled-Plasma-Mass Spectrometry (ICP-MS) at Géosciences Montpellier (France). The preparation and analytical procedures used to determine the geochemistry of the drillsite, shipboard and consortium samples are described below. The main mineralogical characteristics of the studied samples and their major, trace and volatile element concentrations are reported as [Supplementary Dataset S1](#).

1 Sample preparation and bulk geochemical analyses on-board D/V Chikyu

The analytical procedures used to determine the compositions of the 74 drillsite and shipboard samples on-board D/V Chikyu, as well as the precision and accuracy of the methods are reported in detail in the Methods (Phase 1 Leg 2) of [Kelemen et al \[2020\]](#), and summarized as follows.

After removal of potential surface contamination due to drilling and sawing, the samples were rinsed several times in MilliQ water until the water ran clear. Drillsite and shipboard samples were powdered using a bench-top RocklabsTM chrome-steel ring mill (University of Southampton), and a Fritsch Pulverisette 5 Planetary Mill with agate grinding bowls and agate balls (on-board D/V Chikyu), respectively.

Major oxide (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , K_2O , P_2O_5) and trace element (V, Cr, Ni, Cu, Zn, Zr) abundances were measured on a RIGAKU Supermini wavelength dispersive XRF spectrometer equipped with a 200 W Pd anode tube at 50 kV and 4 mA using glass beads and pressed powder pellets respectively. Samples were first ignited at 1000 °C to determine loss on ignition (LOI). Glass beads were prepared by mixing ignited powders with lithium metaborate flux and heating the mixture to 1150 °C using the TK-4100 (Tokyo-Kagaku) automated bead maker. Pressed pellets were prepared with unignited rock powders using a Spex SamplePrep 3630 X-Press. Because on its low concentration in listvenites, serpentinites and ophicarbonates, K_2O was often below detection limit when using beads and, when possible, we reported the values measured on pellets recalculated as volatile free. Shipboard XRF analyses for V, Cr, and Ni were recalibrated using shorebased XRF data acquired on drillsite samples at the University of St. Andrews (UK) following the approach described in [Kelemen et al \[2020\]](#).

The drillsite and shipboard samples were analyzed for total concentrations in H and C (noted TH and TC respectively, also expressed as H_2O and CO_2 in [Supplementary Table S1](#), [Supplementary Dataset S1](#) and [Figure 2](#)) using a Thermo Finnigan Flash EA 112 elemental analyser (EA), with rock powders combusted in an O_2 rich environment within the EA prior to separation by Gas Chromatography. The fraction of carbon present as carbonates (Total Inorganic Carbon, TIC) was determined using a Coulometrics 5012 CO_2 Coulometer coupled to a Carbonate Decomposition Device, in which carbonates from rock samples were dissolved by addition of 2M HCl, thus liberating CO_2 for coulometric titration. TIC values are calculated assuming all carbonates are calcite, efficiently dissolved by HCl. In the listvenite series where no calcite is present, magnesite was not dissolved and we posit that TIC corresponds to the carbon contained in dolomite.

2 Preparation and bulk major element analysis of consortium samples

The 10 consortium samples were prepared for analysis in Lamont Doherty Earth Observatory. First all saw marks were removed with a Dremel tool using an aluminum oxide bit. After saw mark removal samples were scrubbed with a brush in deionized water and dried overnight. Samples were crushed and sieve to separate ~4 mm chips, immediately rinsed with MilliQ water. After drying batches of chips of around 20 gr were powdered in an alumina shatter box for 3 minutes to assure a smooth powder. The shatter box was cleaned with Ottawa sand and rinsed with deionized and MilliQ water between samples.

Major oxides (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , K_2O , P_2O_5 , Cr_2O_3) and a subset of trace elements (Co, Cu, Ni, V and Zn) were analyzed by XRF by GeoLabs (Ontario, Canada). The samples were first run for LOI (105 °C (N atmosphere) then 1000 °C). The ignited samples were then fused with a borate flux to produce the glass beads for analysis. Data obtained annually for Geo Labs' quality control materials are available at <http://www.geologyontario.mndm.gov.on.ca/index.html>.

3 Determination of Fe(II)

The FeO concentrations of 8 serpentinites and 21 Listvenites was quantified at the University of Lausanne (ISTE) following the Fe-titration protocol of [Wilson \[1960\]](#). 200 mg of non-ignited sample powder was dissolved in a $\text{H}_2\text{SO}_4/\text{HF}$ solution with ammonium vanadate (NH_4VO_3) to oxidize and complex all Fe(II) to Fe(III) with vanadium under controlled conditions. The complexed Fe(III) molecules were then reduced and the resulting Fe(II) complexed with a red indicator solution of 2,2'-dipyridil ($\text{C}_{10}\text{H}_8\text{N}_2$) in a $\text{H}_3\text{BO}_3/\text{CH}_3\text{COONa}$ solution. The colored solution was analyzed using a UV/Vis Perkin Elmer Lambda 25 spectrophotometer and the Fe(II) concentration quantified with UV WinLab Software. Calibration was determined from a blank solution and 4 standards having FeO composition of 1.25 wt.% (foid syenite NIM-L), 3.58 wt.% (syenite SY-3), 5.17 wt.% (diorite DR-N) and 8.63 wt.% (gabbro MRG-1). The error on the analyses was below 3 % of the absolute value and the reproducibility on samples and standards was better than 0.1 wt.%.

4 ICP-MS measurement of bulk trace element concentrations

Trace element concentrations (Li, Sc, Ti, V, Mn, Co, Ni, Cu, Ga, As, Mo, Sn, Sb, Rb, Sr, Y, Zr, Nb, Cs, Ba, Rare Earth Elements (REE), Hf, Ta, Pb, Th, U, W, Tl) were determined at Géosciences Montpellier (AETE-ISO, OSU OREME, University of Montpellier, France) using an Agilent 7700X quadrupole ICP-MS. Unignited powder samples were analyzed after the HF/HClO_4 digestion procedure of [Ionov et al. \[1992\]](#) using the measurement protocol described in [Godard et al. \[2000\]](#). Prior to analysis, sample solutions were diluted in a 2% HNO_3 solution to a total dilution of 1000 for serpentinites and listvenites and of 2000 for schists and greenstones. An external calibration was used to determine concentrations for most elements. Nb and Ta concentrations were, in contrast, calibrated with internal standards (Zr and Hf concentrations respectively), a surrogate calibration method adapted from [Jochum et al. \[1990\]](#) to minimize memory effects due to the introduction of concentrated Nb-Ta solutions in the instrument. The Helium cell gas mode of the Agilent 7700X was used to measure Sc, Ti, V, Mn, Co, Ni, Cu, Zn, Ga, As, Sr, Sn and Sb while removing polyatomic interferences. Each ICP-MS measurement is an average of three runs and its precision is determined by the standard deviation. The uncertainty of analysis was estimated for each sample using an error propagation approach, which takes into account the precision of the measurements of (i) the instrumental blank, (ii) the procedural blanks and (iii) the sample analysis. Analyses (i) below

the instrument detection limit, (ii) for which the contribution of the procedural blank is > 70% or (iii) having uncertainties >50 % were eliminated (noted “not determined”). The external precision and accuracy of analyses was assessed by repeated analyses of certified reference materials: serpentinite UB-N, dunite DTS-2b, peridotite JP-1, basalts BIR-1 and BHVO-2, and slate OU-6. The limit of detection of the instrument, the average values of the procedural blanks and rock standards obtained during this study are reported in [Table S1](#).

The concentrations of the subset of elements measured using both ICPMS and XRF were consistent within the instrumental uncertainties, except for Zr that had concentrations significantly lower for the samples from the metamorphic sole when measured by ICPMS compared to XRF. Zr and Hf also showed unexpectedly low values compared to Ti and neighboring elements. This depletion reveals incomplete digestion of Zr-bearing refractory phases, probably zircon, a mineral present in the amphibolites from the metamorphic sole of the Semail ophiolite [[Ishikawa et al., 2005](#); [Rioux et al., 2016](#)]. Zr and Hf were eliminated from the ICPMS dataset for the metamorphic sole at Hole BT1B.

References

- Godard, M., D. Jousset, and J.-L. Bodinier (2000), Relationships between geochemistry and structure beneath a palaeo-spreading centre: A study of the mantle section in the Oman Ophiolite, *Earth Planet. Sci. Lett.*, **180**, 133-148.
- Ionov, D. A., L. Savoyant, and C. Dupuy (1992), Application of the ICP-MS technique to trace element analysis of peridotites and their minerals, *Geostand. Newslett.*, **16**, 311-315.
- Ishikawa, T., S. Fujisawa, K. Nagaishi, and T. Masuda (2005), Trace element characteristics of the fluid liberated from amphibolite-facies slab: Inference from the metamorphic sole beneath the Oman ophiolite and implication for boninite genesis, *Earth Planet. Sci. Lett.*, **240**, 355-377.
- Jochum, K. P., U. Nohl, K. Herwig, E. Lammel, B. Stoll, and A. W. Hofmann (2007), GeoRem: A new geochemical database for reference materials and isotopic standards, *Geostandards and Geoanalytical Research*, **29**(3), 333-338; doi:10.1111/j.1751-1908X.2005.tb00904.x.
- Jochum, K. P., H. M. Seufert, and M. F. Thirwall (1990), High-sensitivity Nb analysis by spark-source mass spectrometry (SSMS) and calibration of XRF Nb and Zr, *Chem. Geol.*, **81**, 1-16.
- Kelemen, P. B., J. M. Matter, D. A. H. Teagle, J. A. Coggon, and the Oman Drilling Project Science Team (2020), *Proceedings of the Oman Drilling Project*, College Station, TX.
- Rioux, M., J. Garber, A. Bauer, S. Bowring, M. Searle, P. Kelemen, and B. Hacker (2016), Synchronous formation of the metamorphic sole and igneous crust of the Semail ophiolite: New constraints on the tectonic evolution during ophiolite formation from high-precision U–Pb zircon geochronology, *Earth and Planetary Science Letters*, **451**, 185-195, doi:<https://doi.org/10.1016/j.epsl.2016.06.051>.
- Wilson, A. (1960), The micro-determination of ferrous iron in silicate minerals by a volumetric and a colorimetric method, *Analyst*, **85**, 823–827.

Text S2. Mass balance calculations

1 Mass balance approach

Mass balance calculations have been carried out using the isocon approach of Baumgartner and Olsen [1995] using a fortran code made available by the authors. The isocon method operates by comparing the composition of a given protolith and altered rock and fitting a line of immobility (an isocon) to a set of elements. The slope and intercept of this line then define the total mass gain or loss of the system. Any element not collinear with the isocon (to within uncertainty) is mobile and either lost or gained from the system. The choice of immobile elements to include in the isocon is subjective and cannot be determined by the fitting scheme. Rather, the fortran code of Baumgartner and Olsen [1995] calculates all possible isocons, corresponding to all combinations of elements which are collinear, to within uncertainty, when plotted. From these we have in each case chosen the isocon with the most elements included since: (a) we expect most elements to be relatively immobile during fluid processes; (b) if a large number of elements are collinear and therefore apparently immobile, it is more likely that this state has arisen because they are indeed immobile than that they have all shown identical patterns of mobility; (c) using this approach the same set of elements consistently appear as immobile where the appropriate protolith of each group is chosen (MMS for Serpentinites and Listvenites I and III, basal/amphibole lherzolites for Listvenite II); (d) including all possible elements rather than subjectively judging X to be immobile is the least subjective approach leading the most comparable results between different protolith-altered rock pairings; and lastly (e) including all possible elements means that all potentially immobile elements contribute to the calculation of the uncertainty of slope/intercept of the line of immobility.

2 Data preparation

Inputs for mass balance calculations consist of the average composition of a potential protolith and the altered rock. These average compositions were specified as log means and standard deviations, since data are log normally distributed for many elements:

$$\log \text{ mean} = \text{mean} [\log_{10}(\text{concentration})]$$

$$\log \text{ SD} = \text{SD} [\log_{10}(\text{concentration})]$$

Regardless of this, in the case of normally distributed data, the log normal mean and standard deviation converge on their normal counterparts. All anhydrous major element data were recalculated to include the contribution of volatiles (measured as LOI) in their totals since volatile elements are considered as mobile components in the mass balance calculation. H₂O and CO₂ were directly measured in BT1B samples while for the Semail ophiolite database we have assumed all LOI constitutes H₂O. Although CO₂ is negligible in serpentinized peridotites, a zero value causes errors with the calculation of log normal statistics so and we have estimated a nominal mean CO₂ of 0.1 wt. % (log mean = -1 ± 0.1) for all protoliths. Similarly, for Listvenite II, all Th data coincidentally had the same value resulting in a standard deviation of 0. To avoid errors this introduced in the code a nominal log standard deviation of 0.3 was given, similar to that of Listvenites I and III. For Serpentinite III there was on one sample for which H₂O and CO₂ were measured directly so these were estimated for other samples using linear regressions of H₂O and CO₂ against LOI from all BT1B samples and the results used to calculate statistics. Data for Na₂O, P₂O₅ were omitted since there were a large number of data below detection limit. XRF bead data for Cr₂O₃, MnO and TiO₂ were omitted in favour of data

from XRF pellets or ICP-MS with the latter always taken where both were available. For Semail ophiolite samples from the literature where ICP-MS trace element data was not available in the Oman ophiolite database, XRF pellet data was substituted where possible (including Sc, Ti, Cr, V, Co, Cu, Zn and Mn). Individual rare-earth elements were not included in the calculations to avoid giving undue weight to this group of elements. Instead, totals for light, middle and heavy rare-earths (LREE, MREE, and HREE) were used in the mass balance calculations.

3. Results of mass balance

The BT1B listvenite series were divided into 3 listvenite domains (Listvenites I-III) and two serpentinites (Serpentinities I and III) from within the upper- and lower-most listvenite groups. For each of these 5 lithological domains, an isocon and associated mass balance calculations were made assuming the protolith had the composition of main mantle section (MMS) Semail peridotites ([Supplementary Table S3](#)).

For listvenite II this provided a pattern of mobility inconsistent with that seen in listvenite I and III and showed non-colinearity for several typically immobile elements including Ni, Cr, Co, SiO₂, MgO, Al₂O₃ on the one hand and LREE, MREE, HREE, Ti, Zr, Hf, and Y on the other. This indicates that, if the protolith for listvenite II was MMS then one of these sets of elements must be quite highly mobile during carbonation, in contrast to the patterns seen in listvenite I and III where all these elements lie collinear (to within uncertainty) and form a single isocon.

An alternative explanation is that the protolith for listvenite II did not have the composition of MMS. To test this, a second mass-balance calculation was made with the composition of basal lherzolites and basal amphibole lherzolites as the protolith ([Supplementary Table S3](#)). Both of these more fertile basal peridotite lithologies were combined in the calculation of an average composition. This was justified on the basis that the exact protolith is unknown and that there are relatively few data for these lithologies. Using a combined average composition of therefore gives a more realistic estimate of the uncertainty in protolith composition and propagates this to calculations of mass gain/loss. With basal peridotites as the protolith, Listvenite II shows a very similar pattern of mobility to listvenites I and III with the majority of element defining a single isocon and pronounced gain of fluid mobile elements including Pb, Cs, Rb, Ba, Li, K₂O and Sr.

References

Baumgartner, L.P., Olsen, S.N. (1995). A least-squares approach to mass transport calculations using the isocon method. *Economic Geology*, 90(5): 1261-1270.

Table S1. Detection limit, procedural blank and trace element concentrations of certified rock standards, serpentinite UB-N, dunite DTS-2b, peridotite JP-1, basalts BIR-1 and BHVO-2, and slate OU-6, determined by Q-ICP-MS at Géosciences Montpellier (AETE-ISO, France). Preferred values were determined from a compilation of literature values downloaded between 2019 and 2020 from <http://georem.mpch-mainz.gwdg.de/> [Jochum *et al.*, 2007]. Note: Mass : Mass used for ICP-MS analysis; DL : Detection Limit of the ICP-MS; Blank: Procedural Blank; σ : standard deviation; Pref.Val.: Preferred values; N: average of N analyses; n.a. : not analyzed; n.d.: not determined.

Table S2. Summary statistics of the compiled composition of the Semail ophiolite mantle section peridotites subdivided by lithotypes; Source of data : main mantle section (MMS) [Gerbert-Gaillard, 2002; Godard *et al.*, 2000; Hanghoj *et al.*, 2010], basal Iherzolites [Lippard *et al.*, 1986; Takazawa *et al.*, 2003] and amphibole bearing basal Iherzolites [Khedr *et al.*, 2014]. Abbreviations: N; number of analyses; Q16 and Q84: 16th and 84th percentiles about the median; SD: Standard deviation.

Table S3. Summary statistics of Oman mantle and BT1B lithologies, recalculated to include volatile components, used in mass balance calculations; Source of data : main mantle section (MMS) [Gerbert-Gaillard, 2002; Godard *et al.*, 2000; Hanghoj *et al.*, 2010], Basal Iherzolites [Khedr *et al.*, 2014; Lippard *et al.*, 1986; Takazawa *et al.*, 2003]. Abbreviations: N; number of analyses; SD: Standard deviation.

Caption for Dataset S1. Mineralogy, major, volatile and trace element composition of Hole BT1B samples.

The rock names and grouping by Units were determined on-board D/V Chikyu from macroscopic observations (Visual Core Description; Kelemen et al. [2020]). Major and trace element concentrations were measured by X-ray fluorescence (XRF). XRF analyses of shipboard and on-site samples noted * in the Method columns were realized on-board D/V Chikyu (Note that major oxide concentrations in Kelemen et al. [2020] are recalculated to 100 wt.%) and those noted † in the Method columns were realized at the University of St. Andrews (see Table BT1-T12 in Kelemen et al. [2020]). XRF analyses of consortium samples were realized at Geolabs. FeO concentrations were measured by titration at the University of Lausanne (Switzerland). Total H and C concentrations (noted TH and TC) were determined on-board D/V Chikyu by combustion CHNS elemental analysis (EA) and used to recalculate H₂O and CO₂ contents. Concentrations of carbon in Ca-carbonates (total inorganic carbon; noted TIC) were determined by coulometry. Trace element compositions were determined using a Quadrupole Inductively-Coupled-Plasma-Mass Spectrometer (Q-ICP-MS) at the University of Montpellier (France). All analyses were performed on samples prepared from non ignited rock-powders, except for XRF major element analyses realized on beads on-board D/V Chikyu. Concentrations are reported in wt.% (10^{-2} g/g) and in ppm (10^{-6} g/g).

Abbreviations: mbg: meters below ground (Chikyu curated depth); Fu-listvenite : fuchsite-bearing listvenite; LOI : Loss on ignition; XRF B : XRF analyses on beads; XRF P : XRF analyses on powder pellets; XRF B/P : XRF major element analyses on beads except for K measured on pellets and recalculated as volatile free; n.a.: not analysed; n.d.: not determined.

(Notes, abbreviations & reference at the bottom of the file)

‡ Sample C5704B-60Z-4-1, 24.0--29.0 cm: Green matrix (Host: Sample C5704B-60Z-4-1, 24.0--29.0 cm - H) crosscut by pink vein (Vein : Sample C5704B-60Z-4-1, 24.0--29.0 cm - V)

Reference : Kelemen, P. B., J. M. Matter, D. A. H. Teagle, J. A. Coggon, and the Oman Drilling Project Science Team (2020), Proceedings of the Oman Drilling Project, College Station, TX.